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THE URANIUM CONTENT OF SOME SPECIMENS OF PHOSPHATE ROCK.

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THE object of this research was to compare some of the more recent methods of measuring the radioactive contents of natural materials by determining either the alpha ray or beta ray emission from a solid surface of the powdered material. For strongly radioactive materials such methods are far more convenient and rapid than the older methods, in which the radon or thoron was first extracted either from a solution of the material or by fusion at high temperature in the case of radon. For the very low activities of most natural rock materials the older methods will still have to be used, although it may be possible in certain cases to use an alpha ray counting method. An emission ray method, also, will only determine the sum of the activities of the combined uranium and thorium families; and some further information must be obtained to enable one to find the absolute uranium and thorium contents of the material.

Three methods were used:—

(*a*) Measurement of the beta ray emission from a thick source of the powdered material with a thin end-window Geiger counter.

(*b*) Measurement of the alpha ray emission under the same conditions with a photomultiplier tube and fluorescent screen.

(*c*) Measurement of the alpha ray emission by exposing a nuclear plate directly to the powder.

DISCUSSION OF THE THREE METHODS.

(*a*) *Beta ray emission.*

A G.E.C. end-window counter, type EHM2, was employed. The window thickness of the counter was 2·1 mg. per sq. cm., and the window diameter 15/16 in. The counter was screened all round with 1 in. of lead with an extra thickness of 1 in. of lead vertically over the counter. The inside of the lead screen was lined with aluminium to prevent any beta rays from the lead entering the counter. The anode of the tube was connected to a 1470 volt stabilised supply, and the cathode

connected to earth through a 1 megohm resister, the output being fed from the cathode via a triode inverter valve to a scale of 64 Los Alamos type 400 scaler. Under these conditions the background count of the counter was about 12 per min., a figure which agrees with the makers' figure for the tube. It was arranged that the powdered material under test could be slid in a metal container to a standard position vertically under the window of the Geiger counter, the front of the lead screen being made detachable for this purpose. The clearance between the surface of the powder in the holder and the counter window was about 2 mm., and the diameter of the holder was considerably greater than the diameter of the window.

To standardise the counter arrangement, a pulp containing 0·10% U_3O_8 in radioactive equilibrium with its products was used. This pulp was kindly supplied to us by Dr. C. F. Davidson of the Atomic Energy Division of the British Geological Survey, to whom our thanks are due. This source gave about 340 counts per min. above the background count, and thus 1 count per min. for a material containing neither thorium nor potassium would correspond to a U_3O_8 content of $2{\cdot}95 \times 10^{-4}\%$. The effect of potassium in the source may be important. It was found that a thick KCl source gave about 138 counts per min. The phosphate materials were, however, specially suitable for the object we had in view, since they are known to contain a negligible amount of potassium and very little thorium. This latter fact was confirmed by our nuclear plate experiments, very few long range Th C′ tracks being found in the exposed plates compared to those due to Ra C′. It will be seen that the background count of about 12 per min. corresponds to a U_3O_8 content of about $3{\cdot}5 \times 10^{-3}\%$, and that the method, therefore, is not suitable for measuring the radioactive contents of ordinary igneous rocks of U_3O_8 contents of perhaps one-tenth of this value. Furthermore, the presence of potassium and thorium will also complicate the interpretation of any results obtained ; for a granite, for instance, most of the beta ray emission will be due to its potassium content.

(*b*) *Alpha ray emission with photomultiplier tube.*

A R.C.A. 5819 photomultiplier tube was used. This is a ten-stage tube, and gives a current amplification of about 6 x 10^5 when operated at 90 volts per stage. The photocathode, which is only very slightly curved and deposited on the inside of the end of the tube, has a diameter of 1·5 in. and an area of about 11·5 sq. cm. The tube and its requisite resistance network were mounted inside a thick-walled light-tight steel tube which acted both as an electrostatic and magnetic screen. The photo-tube had its base upwards and its lower end, which carried the photocathode, projected slightly into a metal light-tight box. A steel holder, containing the powder under test, could be slid directly under the photocathode, or withdrawn to a distance without admitting any light into the system. This enabled one quickly to test the background of the tube.

A zinc sulphide fluorescent powder, type G 86, supplied by the Levy West Laboratories, Wembley, was used for the alpha ray scintillation screen. At first, the powder was fixed directly to the end of the tube by smearing the latter with a little olive oil and scattering a thin layer of powder on it from a fine sieve. This method was, however, found not to be satisfactory. The makers of the tube recommend the cathode to be kept at a negative voltage, and the anode to be led to earth through the desired output anode resistor. If this is done, however, and the fluorescent screen is mounted directly on the tube end, it will also be at the voltage of the cathode. We found that under these conditions the screen was liable to become radioactively contaminated, presumably by collecting fine particles from the sources, under test by electrostatic attraction as the surface of the source were very close to the tube end in order to increase the efficiency of counting. On the other hand, if the cathode is earthed and the anode at the requisite positive potential, the scaler must be fed through a coupling condenser of good quality, and any sudden variations in the anode potential, due to surges in the A.C. power supply, are transmitted directly to the scaler, and may give spurious counts. In a laboratory where comparatively heavy loads may be switched on and off, it is very difficult completely to smooth out these disturbances ; in the end it was found to be best to keep the cathode at a negative potential and to use an independent fluorescent screen placed close to the cathode but not touching it, since this procedure enabled one to mount the screen on an earthed support. It was found that this method of mounting eliminated the trouble due to radioactive contamination ; and, also, that if the screen were not inserted in the apparatus, no counts occurred.

The anode of the photomultiplier was connected to earth via a 1·5 megohm resistor, and the output taken directly from it to the scaler, no amplification being necessary. Under these conditions, the noise signal from the tube was about 25 millivolts and the average alpha ray gave a signal of slightly over 1 volt, the longer range particles giving over 2 volts. The discriminator circuit in the scaler cut off sharply all signals under about 0·75 volt, and it was found that even so it was capable of detecting the emission from samarium oxide, whose alpha rays have a range of 1·5 cm. We can, therefore, conclude that the photomultiplier was capable of detecting a fairly large proportion of the alpha rays emitted from a thick uranium family source.

The background count of the tube was about 15 counts per hour. This count is probably due to slight radioactive contamination of the fluorescent screen since, as already mentioned, it was found that no counts were registered when the screen was removed from the apparatus. This fact shows that neither stray electrical disturbances nor tube background noise were giving counts. A count of 15 per hour corresponds to a U_3O_8 content of $3 \cdot 5 \times 10^{-4}\%$, as determined from the count given by the standard uranium pulp. The photomultiplier counter should, therefore, be capable of measuring the emission from an ordinary granite giving about three alpha particles per cm^2. per hour, since the area of the cathode of the tube is about 11·5 cm^2. It was found that a powdered source of Wicklow granite gave a total

count of 54 in one hour, or a nett count, allowing for background count, of 39 per hour. From nuclear plate measurements the alpha ray rate of emission of the granite was known to be about 3 per cm². per hour, which should give a nett count by the tube of 34·5 per hour, when we take the area of its cathode into account. The scintillation counter can, therefore, measure the U_3O_8 content of such strongly radioactive materials as most rock phosphates with a high degree of accuracy, since a phosphate of 0·0059% U_3O_8 content gives a nett count of about 260 per hour. For weak sources it is, accordingly, a much more accurate method than a beta ray end-window counter. It also has the advantage that it does not count beta rays, and hence its readings are not affected by the potassium content of the source. To obtain accurate measurements from weak sources, such as ordinary rocks, long periods of counting would, however, be necessary in order to reduce the statistical errors below about 5%. It is clear that the background count of the tube would be reduced if the radioactive contamination of the phosphor was less. Some experimenters have obtained lower background counting rates down to 2 or 3 per hour, but they used phototubes with smaller cathodes, so that no real gain in sensitivity was achieved. By testing a large number of fluorescent powder samples one might, however, obtain a more radioactively pure specimen, but the amount of radioactivity necessary to give the present observed count is so small, owing to the radioactive elements being actually incorporated in the phosphor, that such a search would probably be very tedious. It certainly would not have been justified for the measurement of the radioactivity of most phosphates, and was not attempted.

(*c*) *Alpha ray emission with nuclear plates.*

The technique of this method is well known and very simple. A nuclear plate is placed in contact with a plane surface of the powdered material, the emulsion of the plate being in contact with the powder. The exposure time depends on the activity of the source. It was found that an exposure of about three weeks for most of the phosphates gave a convenient number of alpha ray tracks per cm². on the plate. The plate, after processing, is scanned with a 4 mm. dry objective, and the average number of tracks per field observed. Knowing the area of the field of the objective and the exposure time, the alpha ray emission rate per cm². per hour can be calculated.

The theoretical emission rate of a thick source containing only uranium in equilibrium with its products is given by the expression :—

$$p=\tfrac{1}{4}\ \mu d\ N\ C\ \Sigma R,$$

Where,

p = number of alpha tracks emitted per cm². per sec.
μ = range of an alpha ray in the source divided by its range in air.
d = density of the source.
N = the number of alpha rays emitted per sec. per g. of uranium.
C = the uranium content of the source in g. per g.
ΣR = the sum of all the ranges in air of uranium and its products.

In applying this expression to the calculation of actual uranium contents, two uncertainties arise. These are :—

(1) The exact value of μd for the source.

(2) The percentage of the alpha rays, entering the plate, that are counted.

These two points will now be considered.

(1) *The value of μd for the source.*—If the chemical composition of the source is known, μd can be calculated with a fair degree of accuracy from the empirical Bragg-Kleeman Law, that the alpha ray atomic stopping power of an element is proportional to the square root of its atomic weight and is independent of the state of chemical combination of the element. An analysis of one specimen of phosphate from Co. Clare, Ireland, was available, and using this law the calculated value of μd is $1{\cdot}55 \times 10^{-3}$. This figure is not very sensitive to the exact chemical composition of the material used, unless the amount of the heavier elements is considerably increased ; thus, its value for quartz (SiO_2) is $1{\cdot}46 \times 10^{-3}$, whereas for magnetite (Fe_3O_4) it has only increased to $1{\cdot}95 \times 10^{-3}$. We, therefore, took a value of $1{\cdot}55 \times 10^{-3}$ as sufficiently accurate for all the phosphate specimens, since the uncertainty of the results arising under (2) is probably much greater.

(2) *The percentage of the tracks, entering the plate, that are counted.*—For a track to be easily observable in the plate when a 4 mm. dry objective is used, the length of the projection of the track parallel to the surface of the plate must exceed a definite value, which will depend on the acuity of vision of the observer, and, even for the same observer, may vary from day to day. The distribution of the horizontal projections of the tracks from a thick source containing the uranium family in equilibrium has been discussed in a previous paper (1). It was assumed that only alpha particles, whose horizontal range in the plate exceeded 8 mm. air equivalent would be counted. This assumption leads to the result that only 63% of the total theoretical emission of a thick uranium family source will be actually counted. A check on this result was made by exposing a plate to the standard U_3O_8 pulp. If we assume that the stopping power of the pulp is the same as that of quartz, the theoretical total alpha ray emission works out as 425 per cm^2. per hour. The actual count should be 63% of this figure or 268 per cm^2. per hour. The experimental result was 300 per cm^2. per hour, *i.e.* about 10% higher. Most of this discrepancy can probably be attributed to some tracks below the assumed minimum range being counted, although perhaps some of it is due to uncertainty in the exact uranium content of the standard pulp.

The nuclear plate method thus possesses the advantage of being a more or less absolute method, *i.e.* it is not necessary to have a standard source in order to measure, with about 10% accuracy, the uranium content of a uranium family source. It is necessary, on the other hand, to standardise either a Geiger counter or a scintillation counter with a standard source, and the accuracy of these methods depends on the accuracy with which the uranium content of this standard is known. In practice, however, once the apparatus has been set up, either method is much less laborious

and more convenient than the nuclear plate method. The latter method has its uses as a check on the more rapid methods, and can, with care, be used to measure lower uranium contents.

It must be emphasised that the use of all three methods is based on the assumption that the material under test is in radioactive equilibrium with its parent uranium, and if there is any reason for suspecting that this condition is not satisfied further investigations will be necessary. For phosphate rocks, whose age will be measured in at least tens of millions of years, it seems very unlikely that the longer lived members of the uranium family will not be in equilibrium with the parent uranium. It is possible, however, that radon may escape from the surface of the material, and that, consequently, the uranium content as measured by either an alpha or beta ray count will be too low. Thus, it has been found by one of the authors of this paper that the escape of thoron from certain manganese nodules is quite large, a fact which was shown by the use of nuclear plates. These nodules are, however, very porous in structure, and so far we have no reason to suppose that radon escapes from the phosphate rocks to any appreciable extent. Helium geological age measurements also show that the escape of radioactively generated helium from most rocks is very slow, being only appreciable in certain cases after many millions of years. It seems unlikely, therefore, that radon, with a half-life of about four days, could escape from such materials to any serious extent. Unfortunately, if we once grant that radon can diffuse out of the material, it does not follow that the alpha ray surface emission will give a minimum value for the uranium content, equilibrium conditions being assumed. Thus, in the nuclear plate method, the radon which escapes from the source may tend to become concentrated in the small air film between the source and the plate, and in the air spaces at the surface of the powder. This will lead to an excessive alpha ray count, and also to a larger percentage of long-range tracks than a thick source should theoretically give. This latter effect has been observed both by Hurley (2) in America and, also, by various workers in this laboratory (3). Since the beta ray method measures the emission from a thicker layer of the powder, it should suffer less from the uncertainty caused by leakage of radon. It seems to follow, however, that all surface emission methods, while much more convenient and rapid than those based on the measurement of the radon or thoron content of say 6 g. of the material, are inherently not so trustworthy. In many cases, this uncertainty may be small compared with the variations observed between different specimens of the same natural material, and, hence, of no great practical importance.

Comparison of the Results obtained by the Three Methods.

The results obtained by the three methods are given in the following table. They are all based on the assumption that there is no appreciable loss of radon from the sources. For comparison purposes, results on similar specimens due to C. F. Davidson and D. Atkin of the Atomic Energy Division of the Geological Survey, London,

are also included (4). The nuclear plate results are calculated on the assumption that 63% of the total emission is counted, and are, therefore, not based on the standard uranium pulp. They would be about 10% lower if based on the actual count given by this standard. Only a selection of the specimens were measured by this method, since it is rather laborious and was regarded only as a check on the other two methods.

PHOSPHATES.

Specimen	1	2	3	4
Co. Clare, Ireland	0·0186	0·0175	0·0208	0·022
Do.	0·0228	0·0236		0·021
Constantine, Algeria	0·0120	0·0116	0·0106	0·011
Do.	0·0125	0·0115	—	—
Gafsa, Tunisia	0·0047	0·0045	—	0·004
Do.	0·0046	0·0059	0·0048	0·004
Do.	0·0032	0·0045	—	0·005
Egypt, Locality unknown ...	0·0087	0·0107	—	0·010
South Carolina, U.S.A. ...	0·0535	0·0545	0·061	0·054
North Carolina, U.S.A. ...	0·0243	0·0227	—	—
Florida Pebble, U.S.A. ...	0·0216	0·0204	0·021	0·017
Sombrero Island, West Indies ...	—	0·0004	0·0007	—
Grand Cayman Island, West Indies	0·0011	0·0008	—	—
Lower Greensand, England ...	0·0088	0·0092	—	0·008
Upper Greensand, England ...	0·0083	0·0079	—	—
Morrocco, Locality unknown ...	0·0161	0·0160	—	0·016

APATITES.

Norway, Locality unknown ...	0·0093	—	—	0·007
Do.	0·0082	0·0131	0·0093	0·015
Ytterby, Sweden	0·0028	0·0032	—	—
Renfrew, Ontario	0·0057	0·0075	—	—

The figures given are the percentage U_3O_8 content :—

Column 1. From Geiger Counter.
Column 2. From Scintillation Counter.
Column 3. From Nuclear Plates.
Column 4. Davidson's Values.

Where two values for the same material are given, they are for specimens obtained from different sources.

It will be seen that the three methods give reasonably concordant values, and that these agree quite well with Davidson's, which were obtained from different specimens. It will be seen that our values for the African phosphates support Davidson's view that Hébert's (5) results for these rocks are too high, and those due to Guntz too low (6). His values were determined, however, by the fluorescent method of uranium content measurement, and are consequently not based on radioactive methods. The two available specimens from the West Indies gave very low results, showing that these phosphates are of similar origin to the oceanic island phosphates, whose uranium content is also very low. The general problem of the origin of the uranium content of marine phosphates has already been fully discussed by several authors, and for further information on this subject the reader may be referred to the paper by Davidson, which has been already quoted.

In conclusion, we should like to express our thanks to the Geological Department of University College, Dublin, and to Messrs. Goulding for the supply of some of the specimens.

Summary.

The measurement of the uranium content of certain phosphates, using :—

(*a*) A thin end-window Geiger counter.

(*b*) A photomultiplier scintillation counter.

(*c*) Nuclear plates.

is described and the concordance of the results discussed. Phosphate rocks were used, since they are known to contain practically no thorium or potassium, whereas their uranium content is much higher than most naturally occurring materials. It is shown that the agreement between the three methods is reasonably good, but that all these methods may be incorrect if any serious leakage of radon from the powdered source occurs.

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